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Structure and Properties of Rare Earth Praseodymium Coating on the Surface of AZ31B Magnesium Alloy

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Abstract

The poor corrosion resistance of magnesium alloys severely limits the industrial application of magnesium alloys in aerospace as well as automotive applications.Therefore, rare earth coatings were prepared on the surface of magnesium alloys by using a mixture of praseodymium nitrate and potassium ferrocyanide in different concentrations in this study. This impregnation method is simple and green. Considering that without destroying the rare earth coating, in order to enhance the bonding force of the rare earth coating as well as the corrosion resistance, potassium ferrocyanide was taken in this study to pretreat the magnesium alloy first in order to facilitate the obtaining of a better rare earth coating. Scanning electron microscope (SEM) and atomic force microscope (AFM) methods were used to characterize the microscopic morphology of the coatings; Raman and X-ray diffraction (XRD) methods were used to determine the composition and structure of the coatings, electrochemical tests were used to test the corrosion resistance of the coatings. The results show that the pretreatment can enhance the adhesion and hydrophobicity of the coatings. The corrosion resistance of the coating can be controlled by changing the content of rare earth praseodymium and potassium ferricyanide. In this experiment, the optimum process parameters for the composite coating on the surface of AZ31B magnesium alloy were as follows: after pretreatment, the concentration of praseodymium nitrate solution was 0.1 mol/L and the concentration of potassium ferrocyanide was 0.1 mol/L. The processing time was 15 min, and its main compositions were O, Pr, Mg, Fe and P.

Keywords

Praseodymium Nitrate; Potassium Ferricyanide; Corrosion Resistance; Electrochemical Testing.

1. Introduction

Rare-earth conversion films have received more and more attention from researchers in recent years due to their good corrosion resistance and non-toxicity[1]. Rare earth elements are lanthanides, yttrium, scandium, and 17 elements in group IIIB of the periodic table, which have similar atomic structures and similar ionic radii, and are closely symbiotic in nature. Rare earths [2]can be divided into two major groups: light rare earths (lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium) and heavy rare earths (gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, scandium, yttrium)[3]. Rare earths are widely used in the chemical industry, aerospace[4], ceramic materials[5], medicine[6], machinery[7], electronics and other fields because of their excellent optical, electrical, and magnetic properties, as well as their non-toxicity and good biocompatibility[8]. At present, rare earths have been widely used in the materials industry, in which on the one hand, rare earths will be added to steel[9], alloys[10], cast iron, non-ferrous metals[11], which has the effect of grain refinement[12], strengthening the role of

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grain boundaries[13], purification and change the state of inclusions, thereby improving the mechanical properties of the material, including strength, toughness and corrosion resistance[14], but the method of the production process is more complex and costly; on the other hand, rare earths are widely used in metal anticorrosion through chemical immersion, coating, plating and other methods to make steel, cast iron and non-ferrous metal surfaces to form a layer of corrosion resistance and protective function of the coating (plating) layer or conversion film, in order to improve its corrosion resistance. Chromate in the anti-corrosion has a hundred years of history, because of the hexavalent chromium compounds are toxic and environmentally friendly[15], so now has been replaced by non-toxic rare earth conversion film. At present, more rare earth materials used for metal corrosion protection are cerium[16], lanthanum[17], samarium[18], praseodymium and other elements.

In this chapter, the corrosion resistance of magnesium alloys prepared by mixing praseodymium and potassium ferrocyanide is investigated, and the corrosion resistance and corrosion mechanism of the coatings prepared by mixing praseodymium and potassium ferrocyanide are compared with those of the conversion solutions with different concentration ratios. In addition, we compare the performance of coatings prepared with different concentration ratios of the conversion solutions and find new ways to improve them.

2. Experiments

2.1 Materials and Pretreatment

2.1.1 Preparation of Metal Substrate

The substrate used in this study was AZ31 magnesium alloy with the following chemical composition (wt%): 2.89% Al, 0.96% Zn, 0.31% Mn, 0.15% Fe, 0.12% Si and the rest magnesium. The alloys were cut into rectangular specimens of 40mm × 10mm × 1 mm and then sequentially polished with sandpaper coated with silicon carbide with grit sizes ranging from 600#, 800#, 1200#, 1500# to 3000# until the surface was smooth and free of visible scratches.

2.1.2 Coating Preparation

The prepared magnesium alloy specimen was immersed in potassium ferricyanide solution (0.1 mol/L) and reacted for five minutes at room temperature. This process now forms an oxide film on the magnesium alloy. After pretreatment, the specimens were removed from the solution, rinsed with deionized water and dried to obtain a final magnesium alloy specimen with a coated surface.

2.1.3 Preparation of Composite Conversion Membrane

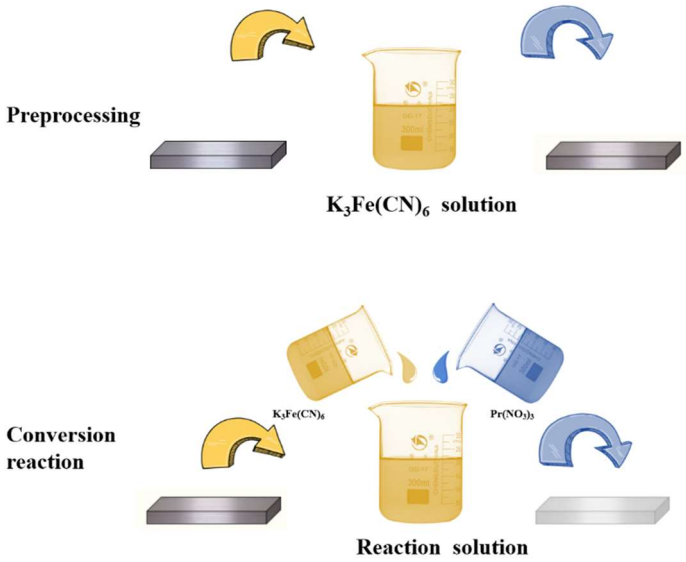

Figure 1. Preparation process of rare earth composite coating

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The conversion conversion solutions were prepared by mixing different concentrations of praseodymium nitrate and potassium ferricyanide. Solution I 0.10 mol/L $Pr(NO_3)_3$ and 0.10 mol/L $K_3Fe(CN)_6$; Solution II 0.1 mol/L $Pr(NO_3)_3$ and 0.05 mol/L $K_3Fe(CN)_6$; Solution III 0.1 mol/L $Pr(NO_3)_3$ and 0.05 mol/L $K_3Fe(CN)_6$; Solution IV 0.05 mol/L $Pr(NO_3)_3$ and 0.05 mol/L $K_3Fe(CN)_6$. The pretreated magnesium alloy specimens were individually immersed in the conversion solution and reacted for 15 minutes in order to carry out the conversion process. After that, the specimens were removed, rinsed with deionized water and dried at room temperature for one hour, thereby forming a composite rare earth transformation coating on the surface of the magnesium alloy. The preparation process of the composite coating on the surface of magnesium alloy is shown schematically in Figure 1.

2.2 Characterization Technique

The surface morphology of the conversion film and the cross-section of the coating were characterized by scanning electron microscopy(SEM), and the elemental composition of the coating was analyzed by X-ray energy spectroscopy (EDS). The phase structure was analyzed by X-ray diffraction (XRD). The test conditions were as follows: phase composition was analyzed in the scanning range of 10° ~ 80° at 8°/min, and the chemical state of the elements in the coating was studied by X-ray photoelectron spectroscopy. Raman was used to study the molecular structure and chemical composition of the coating. A contact angle meter was used to detect the contact angle of the coating. The measurements were performed in air with an accuracy of ±0.5 μ m. Each result given here is the average of three tests. The magnitude of the bond between the coating and the base was tested by a pull-off meter and the experimental results given are the average of three tests.

2.3 Electrochemical Measurements

Electrochemical tests were carried out in an electrochemical workstation in 3.5% NaCl solution of mass fraction. A three-electrode cell was used in the electrochemical tests in which saturated calomel was used as the reference electrode, the sample was used as the working electrode (area of 1 cm^2), and the platinum electrode was used as the counter electrode. The polarization curves were measured at a scanning rate of 2 mV/s. At the end of the test, the polarization curves were fitted with Tafel mode using Corrview software. For electrochemical impedance spectroscopy (EIS) tests, the frequency range was set from 100 kHz to 100 mHz with an interfering signal of 10 mV.All tests were performed at room temperature and each test was performed three times to ensure repeatability and accuracy. The EIS data were fitted using ZView software.

3. Results and Discussion

3.1 Surface and Cross-section Characterization

The samples with different transformation solutions under the same pretreatment conditions were named, and the naming results were as follows:

A1 sample treatment condition: 0.1 mol/L potassium ferricyanide pretreatment, no transformation solution. a2 sample treatment condition: 0.1 mol/L potassium ferricyanide pretreatment, transformation solution 1. a3 sample treatment condition: 0.1 mol/L potassium ferricyanide pretreatment, transformation solution 2. a4 sample treatment condition: 0.1 mol/L potassium ferricyanide pretreatment, transformation solution 3. a5 sample treatment Conditions: 0.1 mol/L potassium ferricyanide pretreatment, transformation solution 4.

Figure 2 shows the microscopic morphology of sample coatings prepared from magnesium alloys under different conversion conditions. The preparation of the composite coating requires the preparation of a pretreatment film on the surface of the magnesium alloy to control the conversion rate of the rare earth coating, and finally a relatively uniform sample coating is obtained. Figure 2(a1) is a 100 um SEM image of the A1 sample, from which it is obvious to see the polishing marks on the magnesium alloy, which is due to the thin layer of magnesium hydroxide film generated in the

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pretreatment process, so it is obvious to see the metal base state, which is in line with the initial design of the pretreatment.

Figure 2(b1)(c1)(d1)(e1) shows the samples prepared under different transformation conditions. From the micro-morphology of the sample coatings, when the rare earth praseodymium nitrate content in the transformation solution is the same, the scanning diagrams of samples A2 and A3 (b1)(c1) show that the coatings of sample A2 are more homogeneous and compact. The surface coating of sample A3 is more agglomerated and less homogeneous, probably because of the lower content of potassium ferricyanide as oxidizing agent, which has a greater influence on the formation of the coating, resulting in the magnesium alloy coating with larger cracks and poorer inhomogeneous properties.

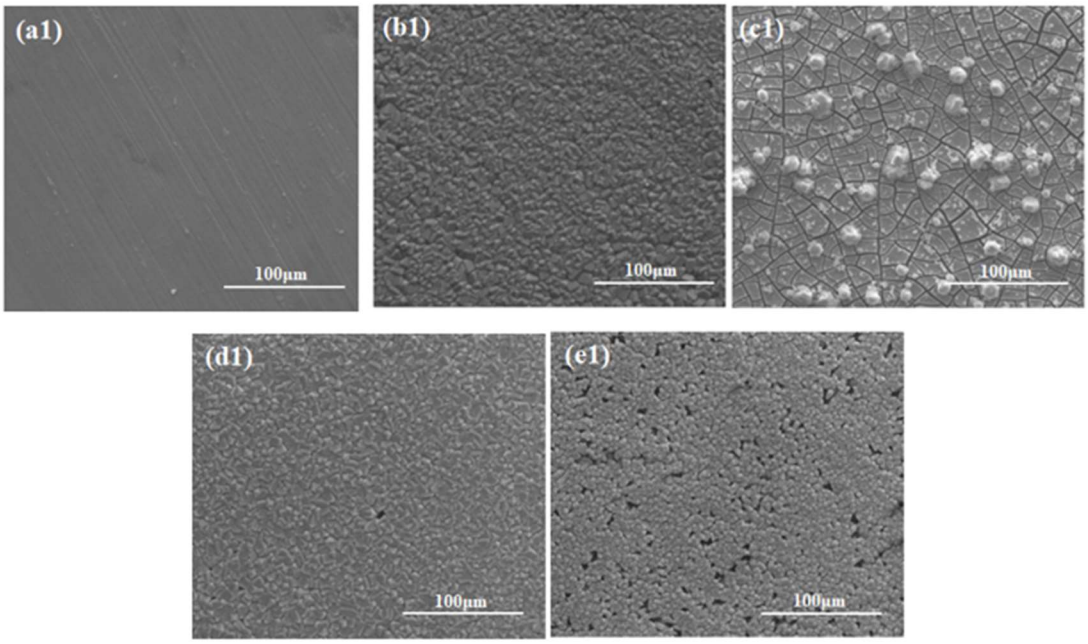

Figure 2. (a1) SEM of A1 sample at different scales (b1) SEM of A1 sample at different scales; (c1) SEM of A3 at different scales; (d1) SEM of A4 at different scales; (e1) SEM of A5 at different scales

From the composition of sample A2 (pretreated with 0.1 mol/L potassium ferrocyanide, the conversion solution is 0.1 mol/L praseodymium nitrate: 0.1 mol/L potassium ferrocyanide) in Figure 3, it can be seen that the main components of the coating are composed of C, N, O, K, Pr, and Fe. From previous related studies, it is known that rare earth praseodymium can play a role in grain refinement, formation of stable passivation film and reduction of impurity elements, which corresponds to the SEM and EDS results in this study.

3.2 Raman and XRD Characterization Results of Composite Coatings

Figure 3 (a) shows the Raman test results of samples A1, A2, A3, A4, and A5 from 50 cm-1 to 4000 cm-1, from which it can be seen that all composite coatings have more prominent peaks between 2000 cm^{-1} and 2250 cm^{-1}, except for only the pretreated samples. These peaks were then compared with the Raman spectra of potassium ferricyanide and potassium ferrocyanide tests, and it can be seen from Figure. 3 (b) that the peaks in Figure (a) correspond to potassium ferrocyanide, which indicates that potassium ferricyanide and praseodymium nitrate reacted with each other during the formation of the composite coatings, a part of the potassium ferricyanide was reduced to potassium ferrocyanide, which, in combination with the EDS results of the Coating A2, shows that a part of the rare-earth Pr should be combined with potassium ferricyanide, and the other part formed praseodymium hydroxide, a hydrate of Pr.

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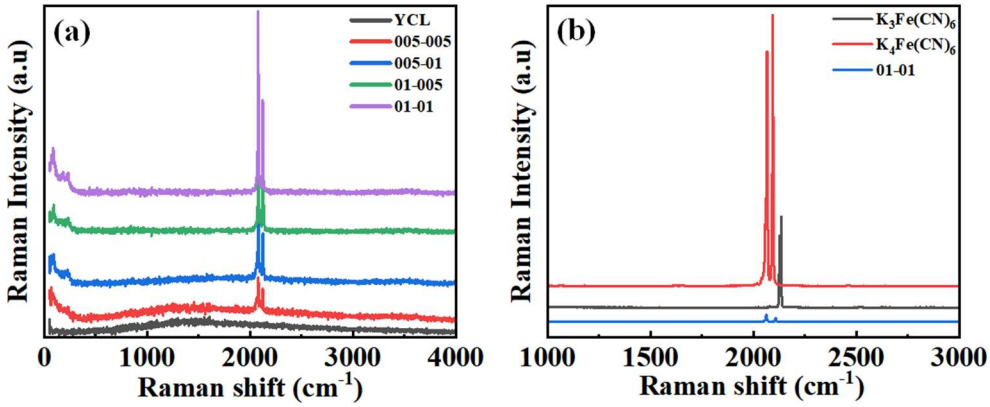

Figure 3. (a) Raman results of samples A1, A2, A3, A4, A5 (b) Raman results of A2 and potassium ferricyanide and potassium ferrocyanide

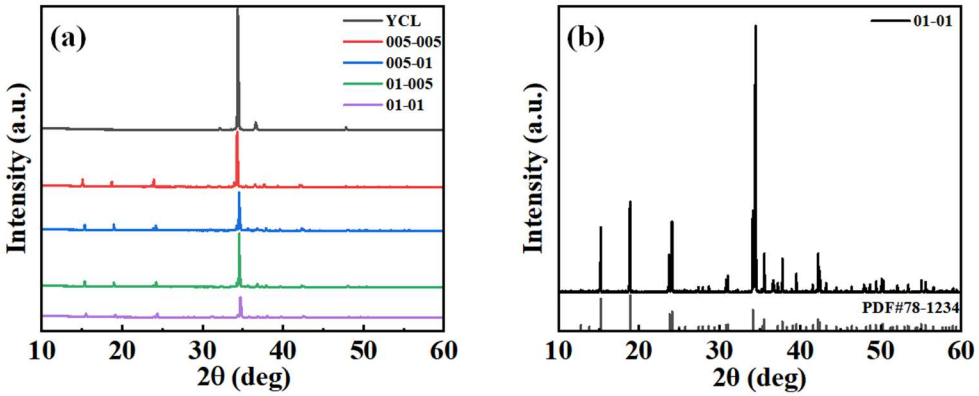

Figure 4. (a) XRD results of samples A1, A2, A3, A4, A5 (b) Comparison between XRD of A2 and standard card PDF#78-1234

To further elucidate the composition of the coatings, the samples were subjected to XRD. The XRD results for five samples prepared with different concentrations of paved nitrate and potassium ferrocyanide are shown in Figure 4 (a) The XRD spectra indicate the presence of $KPrFe(CN)_6$ in the composite coatings, which has been corroborated by the standardized card PDF#78-1234 in Figure 4 (b). This phase identification indicates that praseodymium is incorporated into the coating in the form of praseodymium hexacyanoferrate, a compound that contributes to the stability and protective properties of the coating.

3.3 Corrosion Resistance Test Results of Composite Coatings

Figure 5(a) demonstrates the open-circuit potential of composite coatings of AZ31B magnesium alloy prepared in different cerium nitrate and potassium ferricyanide conversion solutions after potassium ferricyanide pretreatment. The electrochemical open-circuit test results show that the open-circuit potentials of the composite coating samples are all shifted upwards with significant potential improvement. The best sample is the coating of the system of 0.1 mol/L cerium nitrate and 0.1 mol/L potassium ferricyanide, with an open-circuit potential of -0.95 V. Compared with the blank magnesium alloy, the open-circuit potential of -1.60 V is greatly improved, so the composite coating of the magnesium alloy has an obvious effect in the direction of corrosion prevention.

Figure 5(b) shows the polarization curves of the composite coatings formed on AZ31B magnesium alloy pretreated with potassium ferricyanide in different concentrations of cerium nitrate and potassium ferricyanide conversion solutions. The results of electrochemical tests showed that the pretreated specimens exhibited a more positive corrosion potential in comparison with the blank substrate specimens in 3.5% NaCl solution, showing stronger corrosion performance. The system

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containing 0.1 mol/L cerium nitrate with 0.1 mol/L potassium ferricyanide performed particularly well, with the largest positive shift in corrosion potential, while maintaining the lowest corrosion current density value of the system, which is five orders of magnitude lower than that of the untreated blank magnesium alloy specimen. This is mainly attributed to the reaction of rare-earth praseodymium ions (Pr^{3+}) with ferrocyanide at the metal/solution interface. On the one hand, Pr^{3+} is preferentially deposited in the cathode region to form $Pr(OH)_3$ and PrO_2 particles; on the other hand, ferrocyanate undergoes a redox reaction that oxidizes the trivalent Pr into the tetravalent state to produce rare-earth insoluble species. This suggests that composite coatings with these specific concentrations provide the strongest corrosion protection, probably due to the effective inhibition of the cathodic reaction by the rare earth ions, which also contribute to the reduction of Ecorr.

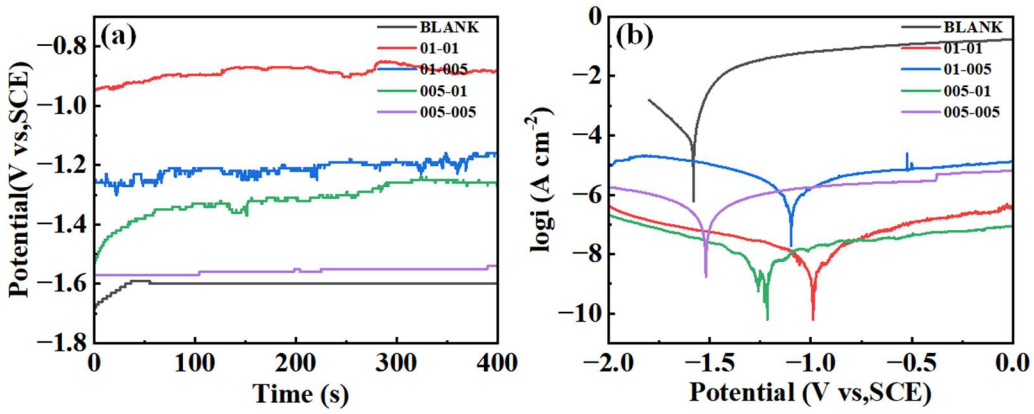

Figure 5. (a) Open-circuit potential of each specimen, (b) Polarization curves of each specimen

3.4 Protective Mechanisms of Composite Coatings

The rare earth element praseodymium has a unique is electronic structure and chemical activity, so it can play a great role in the corrosion prevention of alloys. The results of the present experimental study are in agreement with those of most researchers. Praseodymium is involved in the formation of stable oxides or hydroxides (e.g., Pr_2O_3, $Pr(OH)_3$) during the coating process, which fills up the micropores and cracks in the coating and forms a denser protective layer. This finding is consistent with the scanning results in this study, where praseodymium contributes to the formation of a denser coating to protect the magnesium alloy substrate. The dense structure of this composite film can effectively fill the loose pores of the conventional MgO film and impede the penetration of corrosive media (e.g., Cl-), thus inhibiting localized pitting and galvanic coupling corrosion. For example, similar to the role of cerium (Ce), praseodymium-containing composite oxide films may significantly reduce the corrosion rate by a similar mechanism praseodymium compounds act as cathodic or anodic inhibitors during corrosion, slowing down the rate of electrochemical reactions. For example, Pr^{3+} ions migrate to defects in the electrolyte to form passivation films. The electrochemical results are consistent with those tested in this study. Praseodymium is able to form stable intermetallic compounds with impurity elements (e.g., Fe, Ni, etc.) in magnesium alloys, which reduces the solid solubility of the impurities in the matrix, thus weakening their activity as a cathodic phase. In addition, praseodymium may inhibit the cathodic hydrogen precipitation reaction and slow down the corrosion kinetic process through surface passivation. Although there are fewer specific studies on praseodymium in the existing literature, based on mechanistic analogies with other rare earth elements (e.g., Ce, Y), it can be hypothesized that praseodymium acts in magnesium alloy coatings through a similar pathway.

4. Conclusion

(1) In this study, cerium-based conversion coatings were successfully formed on the surface of AZ31B magnesium alloy using cerium nitrate and potassium ferricyanide solutions. After phytic acid

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pretreatment, the coatings showed uniform morphology, strong adhesion and significantly improved corrosion resistance. In this process, comparing the results of the samples prepared by different processes, the following conclusions were obtained: the largest capacitive arc diameter was observed in the coatings treated with 0.1 mol/L praseodymium nitrate and 0.1 mol/L potassium ferricyanide, and the corrosion resistance was the best. The corrosion current was improved by about 5 orders of magnitude.

(2) The coatings prepared without potassium ferricyanide pretreatment had smaller contact angles and the composite coatings had higher hydrophobicity, which ensured the coatings' corrosion resistance in the face of some harsh environments in nature.

(3) Among the composite coatings, the coating treated with the conversion solution of 0.1 mol/L praseodymium nitrate and 0.1 mol/L potassium ferricyanide has the smallest crystalline particles, and the surface integrity of the coatings is the best, with no large pores and cracks.

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